STABILIZED PHOSPHATE ESTER-BASED FUNCTIONAL FLUID COMPOSITIONS

This is a continuation in part of Ser. No. 07/897,189 filed Jun. 11, 1992, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to phosphate ester functional fluids and more particularly to phosphate ester fluids of improved thermal, hydrolytic and oxidative stability useful as aircraft hydraulic fluids.

Functional fluids have been utilized as electronic coolants, diffusion pump fluids, lubricants, damping fluids, bases for greases, power transmission and hydraulic fluids, heat transfer fluids, heat pump fluids, refrigeration equipment fluids, and as a filter media for air-conditioning systems. Hydraulic fluids intended for use in the hydraulic system of aircraft for operating various mechanisms and aircraft control systems must meet stringent functional and use requirements. Among the most important requirements of an aircraft hydraulic fluid is that it be stable against oxidative and hydrolytic degradation at elevated temperatures.

In use, aircraft hydraulic fluids commonly become contaminated with moisture. Water enters the hydraulic system with air bled from an engine compressor stage. During operations, the moisture level in Type IV aircraft hydraulic fluids normally ranges from about 0.2 to about 0.35% by weight. Water causes hydrolytic decomposition of phosphate esters to produce partial esters of phosphoric acid. Hydrolytic breakdown of the ester is accelerated if water content exceeds about 0.5% by weight. Conventionally, phosphate ester aircraft hydraulic fluids are formulated to contain an acid scavenger which neutralizes partial esters of phosphoric acid released by hydrolytic breakdown of the triester. Over time, however, the acid scavenger becomes depleted and organometallic compounds are formed by complex reactions involving the phosphate triester, phosphoric acid partial esters, and surfaces of the metal environment within which the hydraulic fluid is ordinarily contained. These organometallic compounds, of which iron phosphate is usually the most prominent by-product, are not soluble in the hydraulic fluid.

Higher performance aircraft are operated under conditions which expose hydraulic fluids to increasing temperatures. Current Grade A fluids operate at maximum temperatures in the range of 225 to 240° F. However, projected aircraft applications will expose aircraft hydraulic fluids to bulk fluid temperatures in the range of 275° F. or higher. At such temperatures, the potential for oxidative and hydrolytic breakdown of phosphate esters is substantially increased.

Degradation of phosphate ester hydraulic fluids is also accelerated where the fluids are exposed to compressed air. The rate of air oxidation of such fluids also increases with temperature. Thus, for application at 275° F. or higher, a need exists for fluids of both enhanced thermal oxidative stability and enhanced thermal hydrolytic stability.

Erosion problems may also be expected to increase with bulk fluid temperature. Erosion is a form of electrochemical corrosion, more precisely referred to as zeta corrosion, the rates of which are increased with temperature. The incidence of cavitation, which is one of the mechanical sources of erosion problems, is also likely to increase with temperature. As erosion progresses, the presence of metallic or other insoluble components may result in filter clogging and replacement, and can cause a change in the physical and

chemical properties of the fluid, thereby requiring premature draining of fluids from the system. Metal contaminants also reduce oxidative stability of the fluid, accelerating corrosion. In addition to any effects resulting from contamination by metal (or other) contaminants, the fluid may suffer deterioration in numerous other ways, including: a) viscosity change; b) increase in acid number; c) increased chemical reactivity; and d) discoloration.

A hydraulic fluid useful in aircraft is available from applicants' assignee under the trademark Skydrol® LD-4. This composition contains 30 to 35% by weight dibutyl phenyl phosphate, 50 to 60% by weight tributyl phosphate, 5 to 10% of viscosity index improvers, 0.13 to 1% of a diphenyldithioethane copper corrosion inhibitor, 0.005% to about 1% by weight, but preferably 0.0075% to 0.075% of a perfluoroalkylsulfonic acid salt antierosion agent, 4 to 8% by weight of an acid scavenger of the type described in U.S. Pat. No. 3,723,320 and about 1% by weight of 2,6-di-tertiary-butyl-p-cresol as an antioxidant. This composition has proved highly satisfactory in high performance aircraft application. However, it was not designed for extended operations at temperatures in the range of 275° F.

SUMMARY OF THE INVENTION

Among the several objects of the present invention, therefore, may be noted the provision of an improved functional fluid useful as a hydraulic fluid in aircraft applications; the provision of such a fluid which exhibits improved hydrolytic stability, especially at elevated temperatures; the provision of such a fluid which exhibits improved oxidative stability at elevated temperatures; the provision of such a fluid which exhibits advantageous viscosity characteristics and especially viscosity stability under shear conditions; the provision of such a fluid of relatively low density; the provision of such a fluid which has not only high resistance to oxidation but also low toxicity; the provision of such a composition which has improved anti-erosion properties; and the provision of such a fluid composition which exhibits improved resistance to corrosion of metal components of an aircraft or other hydraulic fluid system.

Briefly, therefore, the present invention is directed to a fluid composition suitable for use as an aircraft hydraulic fluid. The composition comprises a fire resistant phosphate ester base stock, the base stock comprising between about 10% and about 100%, preferably between about 20% and about 99%, by weight of a trialkyl phosphate, between about 0% and about 70% by weight of a dialkyl aryl phosphate, and from about 0% to about 25% by weight of an alkyl diaryl phosphate, with the proviso that the sum of the proportionate amount of each base stock component must equal 100%. The alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate contain between 3 and 8 carbon atoms, preferably between 4 and 8 carbon atoms, more preferably between 4 and 5 carbon atoms, and are bonded to the phosphate moiety via a primary carbon. It is still further preferred that the alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate are isoalkyl groups. In a preferred embodiment, the base stock of the composition comprises between about 50% and about 85% by weight of a trialkyl phosphate, between about 18% and about 35% by weight of a dialkyl aryl phosphate, and from 0 to about 5% by weight of an alkyl diaryl phosphate. In addition to the fire resistant base stock, the composition further comprises an acid scavenger in an amount effective to neutralize phosphoric acid

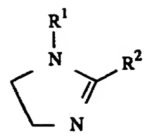
partial esters formed in situ by hydrolysis of any of the phosphate esters of the base stock; an anti-erosion additive in an amount effective to inhibit flow-induced electrochemical or zeta corrosion of the flow metering edges of hydraulic servo valves in hydraulic systems; a viscosity index improver in an amount effective to cause the fluid composition to exhibit a viscosity of at least about 3.0 centistokes (cst) at about 210° F., at least about 9.0 centistokes at about 100° F., and less than about 4200 centistokes at −65° F.; and an anti-oxidant in an amount effective to inhibit oxidation of fluid composition components in the presence of oxygen.

Preferably, as previously indicated, the alkyl substituents of the trialkyl phosphate, dialkyl aryl phosphate, and the alkyl diaryl phosphate contain between 4 and 8 carbon atoms, more preferably between 4 and 5 carbon atoms. It is still further preferred that the alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate are isoalkyl groups. Most preferably, therefore, the alkyl substituents are isoalkyl C_4 and C_5 groups, namely, isobutyl and isopentyl (also known as isoamyl), respectively.

The invention is further directed to a fluid composition suitable for use as an aircraft hydraulic fluid and containing a novel combination of additives. The composition comprises a fire resistant phosphate ester base stock comprising between about 10% and about 90% by weight of a trialkyl phosphate, between about 0 and about 70% by weight of a dialkyl aryl phosphate and from 0% to about 25% by weight of an alkyl diaryl phosphate. The alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate contain between 3 and 8 carbon atoms, preferably between 4 and 8 carbon atoms, more preferably between 4 and 5 carbon atoms and are bonded to the phosphate moiety via a primary carbon atom. It is still further preferred that the alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate are isoalkyl groups. The composition further comprises a viscosity index improver in a proportion, on a solids (methacrylate polymer, as hereinafter described) basis, of between about 3% and about 10% by weight of the composition. The viscosity index improver comprises a methacrylate ester polymer, the repeating units of which substantially comprise butyl and hexyl methacrylate, at least 95% by weight of the polymer having a molecular weight of between about 50,000 and about 1,500,000. The viscosity index improver is conveniently employed or provided in the form of a solution in a phosphate ester solvent, preferably a trialkyl phosphate ester, such as, for example, tributyl or triisobutyl phosphate, or a combination of alkyl and aryl phosphate esters. In a preferred embodiment, the phosphate ester solvent is comprised of one or more of the phosphate ester components which constitute the phosphate ester base stock of choice. In such manner, the phosphate ester solvent becomes in effect part of the base stock, and the stated ranges of suitable proportions of phosphate esters hereinafter described reflect the phosphate ester(s) added as a carrier or vehicle for the viscosity index improver. The composition further comprises an anti-erosion agent in a proportion of between about 0.02% and about 0.08% by weight of the composition, the anti-erosion agent comprising an alkali metal salt of a perfluoroalkylsulfonic acid, the alkyl substituent of which is hexyl, heptyl, octyl, nonyl or decyl. The composition comprises an acid scavenger in a proportion of between about 1.5 and about 10% by weight of the composition, the acid scavenger comprising a derivative of 3,4-epoxycyclohexane carboxylate or a diepoxide compound of the type disclosed in U.S. Pat. No. 4,206,067. The composition further contains a 2,4,6-trialkylphenol in a proportion of between about 0.1% and about 1% by weight, a di(alkylphenyl)amine in a proportion of between about 0.3% and about 1% by weight, and a hindered polyphenol compound selected from the group consisting of bis(3,5-dialkyl-4-hydroxyaryl)methane, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxyaryl)benzene and mixtures thereof in a proportion of between about 0.3% and about 1% by weight of the composition. The alkyl substituents of trialkyl phosphate and dialkyl aryl phosphate are preferably butyl or pentyl.

The invention is further directed to a fluid composition suitable for use as an aircraft hydraulic fluid comprising a fire resistant organophosphate ester base stock. The base stock comprises between about 10% and about 100%, preferably between about 20% and about 99%, by weight of a trialkyl phosphate wherein the alkyl substituents are substantially isoalkyl C_4 or C_5, between about 0% and about 70% by weight of a dialkyl aryl phosphate wherein the alkyl substituents are substantially isoalkyl C_4 or C_5, and between about 0% and about 25% by weight of an alkyl diaryl phosphate wherein the alkyl substituent is substantially isoalkyl C_4 or C_5. The composition further comprises an acid scavenger in an amount effective to neutralize phosphoric acid and phosphoric acid partial esters formed in situ by hydrolysis of any of the phosphate esters of the base stock; an anti-erosion additive in an amount effective to inhibit flow-induced electrochemical corrosion of the flow metering edges of hydraulic servo valves in hydraulic systems; a viscosity index improver in an amount effective to cause the fluid composition to exhibit a viscosity index of at least about 3.0 centistokes at about 210° F., at least about 9.0 centistokes at about 100° F., and less than about 4200 centistokes at about −65° F.; and an antioxidant in an amount effective to inhibit oxidation of fluid composition components in the presence of oxygen.

The invention is further directed to a fluid composition suitable for use as an aircraft hydraulic fluid comprising a phosphate ester base stock. The base stock comprises between about 10% and about 100%, preferably between about 20% and about 99%, by weight of a trialkyl phosphate wherein the alkyl substituents are substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), between about 0% and about 70% by weight of a dialkyl aryl phosphate wherein the alkyl substituents are substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely isobutyl or isopentyl), and between about 0% and about 25% by weight of an alkyl diaryl phosphate wherein the alkyl substituent is substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely isobutyl or isopentyl). The composition further comprises an acid scavenger in an amount effective to neutralize phosphoric acid partial esters formed in situ by hydrolysis of any of the phosphate esters of the base stock; an anti-erosion additive in an amount effective to inhibit flow-induced electrochemical or zeta corrosion of the flow metering edges of hydraulic servo valves in hydraulic systems; a viscosity index improver in an amount effective to cause the fluid composition to exhibit a viscosity index of at least about 3.0 centistokes at about 210° F., at least about 9.0 centistokes at about 100° F., and less than about 4200 centistokes at −65° F.; an antioxidant in an amount effective to inhibit oxidation of fluid composition components in the presence of oxygen; and a 4,5-dihydroimidazole compound in an amount effective to decrease by at least about 25% the rate of breakdown at 300° F. of phosphate triesters in the composition to phosphoric acid partial esters, as measured by epoxide depletion. The 4,5-dihydroimidazole compound corresponds to the formula



where R^1 is hydrogen, alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl, alkoxyalkyl or alkoxyalkenyl, and R^2 is alkyl, alkenyl or an aliphatic carboxylate. The invention is further directed to a fluid composition suitable for use as an aircraft hydraulic fluid comprising a fire resistant phosphate ester base stock. The base stock comprises between about 10% and about 100%, preferably between about 35% and about 99%, by weight of a trialkyl phosphate, between about 0% and about 35% by weight of a dialkyl aryl phosphate, and between about 0% and about 20% by weight of a triaryl phosphate. The alkyl substituents of the trialkyl phosphate and the dialkyl aryl phosphate contain between 3 and 8 carbon atoms, preferably between 4 and 8 carbon atoms, more preferably between 4 and 5 carbon atoms and are bonded to the phosphate moiety via a primary carbon. It is still further preferred that the alkyl substituents of the trialkyl phosphate and the dialkyl aryl phosphate are isoalkyl groups. The aryl substituents of the dialkyl aryl phosphate esters and the triaryl phosphate esters are typically phenyl, but may also be an alkyl-substituted phenyl (alkylphenyl) wherein the alkyl substituent is C_1 to C_9, preferably C_3 to C_4. Nonlimiting examples of the alkyl-substituted phenyl substituents include tolyl (also known as methylphenyl), ethylphenyl, isopropylphenyl, isobutylphenyl, tert-butylphenyl, and the like. The fluid composition further comprises an acid scavenger in an amount effective to neutralize phosphoric acid and phosphoric acid partial esters formed in situ by hydrolysis of any of the phosphate esters of the base stock, an anti-erosion additive in an amount effective to inhibit flow-induced electrochemical or zeta corrosion of the flow metering edges of hydraulic servo valves in hydraulic systems; a viscosity index improver in an amount effective to cause the fluid composition to exhibit a viscosity of at least about 3.0 centistokes at about 210° F., at least about 9.0 centistokes at about 100° F., and less than about 4200 centistokes at −65° F.; and an antioxidant in an amount effective to inhibit oxidation of fluid composition components in the presence of oxygen.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. **1** to **12** are plots of epoxide depletion versus time for hydraulic fluid formulations tested under varying conditions of temperatures, moisture content, and other parameters; and

FIG. **13** is a bar graph illustrating the superior anti-corrosion properties of the functional fluid of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, it has been discovered that a hydraulic fluid of improved thermal, hydrolytic, and oxidative stability is provided by utilizing a phosphate ester base stock which contains a high concentration of alkyl ester moieties and contains relatively small proportions of phenyl or other aryl esters.

The base stock comprises a mixture of trialkyl phosphate and dialkyl aryl phosphate, in each of which the alkyl substituents are C_5 to C_8, preferably C_4 to C_8, more preferably C_4 r C_5, and are bonded to the phosphate moiety via a primary carbon. It is still further preferred that the alkyl substituents of the trialkyl phosphate and the dialkyl aryl phosphate are isoalkyl groups. Optionally, the base stock further comprises a small proportion of alkyl diaryl phosphate wherein the alkyl substituent is as previously defined. Further advantages are realized if the alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate esters are primarily comprised of isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), in preference to the normal isomers thereof. In this preferred instance also, attachment of the alkyl substituent to the phosphate should be via a primary carbon atom.

In addition to the improved base stock, the composition of the invention preferably contains a combination of additives which further enhances the properties of the fluid as compared to fluids previously available in the art for use in the aircraft hydraulic systems. Moreover, it has been found that the additive combinations of this invention are effective in enhancing the properties of base stock compositions previously known in the art or otherwise differing from the preferred base stock of the functional fluids of this invention. But the most advantageous properties are realized using both the additive package and the base stock of the invention. This is particularly true where the alkyl substituents of the trialkyl phosphate, the dialkyl aryl phosphate, and the alkyl diaryl phosphate, especially the trialkyl phosphate and the dialkyl aryl phosphate, are isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl).

In a preferred embodiment, the base stock is characterized by a very low alkyl diaryl phosphate ester content, preferably not more than about 5% by weight, more preferably not more than about 2% by weight. It is further preferred that the sum of the proportions of esters containing an aryl substituent, i.e., dialkyl aryl, alkyl diaryl, and triaryl phosphates, does not constitute more than about 25% by weight of the base stock.

More particularly, in a preferred embodiment, the base stock composition advantageously comprises between about 50% and about 85% by weight of a trialkyl phosphate wherein the alkyl substituents are substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), between about 18% and about 35% by weight of a dialkyl aryl phosphate wherein the alkyl substituent is substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), and from 0 to about 5% by weight of an alkyl diaryl phosphate wherein the alkyl substituent is substantially C_4 or C_5, preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl). Preferably the aryl substituents are phenyl and alkyl-substituted phenyl (alkylphenyl) wherein the alkyl substituent is C_1 to C_9, more preferably C_3 to C_4. Non-limiting examples of the alkyl-substituted phenyl include tolyl, ethylphenyl, isopropylphenyl, isobutylphenyl, tert-butylphenyl, and the like, with tert-butylphenyl generally being more preferred. As contrasted, for example, with Skydrol® LD-4 hydraulic fluid, which has a significantly higher diaryl (as diphenyl) ester content, the base stock of the functional fluid of the present invention exhibits significantly improved hydrolytic stability at temperatures substantially above 225° F. using the same acid scavenger system as that incorporated into LD-4. Using the same anti-oxidant additive as LD-4, a composition comprising the base stock of the present invention exhibits significantly enhanced thermal, oxidative, and hydrolytic stability. As a result of the relatively low diaryl ester content of the base stock, the functional fluid of the present invention has

relatively low density, which is advantageous in aircraft hydraulic fluid applications.

In the preferred base stock of the present invention, it is particularly preferred that the alkyl substituents be isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), most preferably isoalkyl C_4 (isobutyl). It has been found that a base stock composition comprising triisobutyl phosphate or triisopentyl phosphate and diisobutyl phenyl phosphate or diisopentyl phenyl phosphate affords multiple advantages as compared to the same compositions in which the alkyl substituents are n-butyl or n-pentyl.

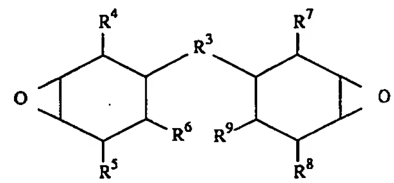
TABLE A

	TBP	TIBP
Oral LD_{50}	1200 mg/kg	>5000 mg/kg
Dermal LD_{50}	>10,000 mg/kg	>5000 mg/kg
Eye Irritation	Mildly irritating	Practically non-irritating
Skin Irritation	Severely irritating	Moderately irritating
Subchronic		
Bladder Hyperplasia	In rats >1000 ppm In rats >5000 ppm NOEL 200 ppm	None observed NOEL 5000 ppm
Hen Neurotox	Not neurotoxic Tested at LD_{50} = 1500 mg/kg	Not neurotoxic Tested at LD_{50} = >5000 mg/kg
Genotoxicity	Ames - negative CHO/HGPRT - negative in vitro cytogenetics - negative in vivo cytogenetics - negative	Ames - negative Mouse micronucleus - negative

In addition, in the context of the present invention, the phosphate esters wherein the alkyl substituents attached to the phosphate moiety are isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl) have further been found to exhibit hydrolytic stability superior to that exhibited by the corresponding normal alkyl phosphate esters at the high temperatures to which the hydraulic systems of high performance aircraft are exposed. The realization of this advantage occurs in the absence of any adverse effects upon seal integrity. That is, isobutyl and isopentyl esters maintain the same high level of seal integrity exhibited by normal alkyl phosphate esters. Or stated differently, the materials of which hydraulic system seals are commonly fabricated have been found to maintain a level of swelling when in contact with the isoalkyl esters that is equivalent to that experienced when in contact with the corresponding normal alkyl esters. Moreover, it has been found that the isobutyl and isopentyl esters are even lower density than the normal alkyl esters, which means that the weight of fluid in a given aircraft hydraulic system is lower, resulting in improved aircraft fuel efficiency.

In addition to the improved base stock, the composition of the invention preferably contains a combination of additives which further enhances the properties of the fluid as compared with fluids previously available in the art for use in aircraft hydraulic systems.

More particularly, the composition incorporates an acid scavenger in a proportion sufficient to neutralize phosphoric acid and phosphoric acid partial esters formed in situ by hydrolysis of components of the phosphate ester base stock under conditions of the service in which the hydraulic fluid composition is used. Preferably, the acid scavenger is a 3,4-epoxycyclohexane carboxylate composition of the type described in U.S. Pat. No. 3,723,320. Also useful are diepoxides such as those disclosed in U.S. Pat. No. 4,206,067 which contain two linked cyclohexane groups to each of which is fused an epoxide group. Such diepoxide compounds correspond to the formula:



wherein R^3 is an organic group containing 1 to 10 carbon atoms, from 0 to 6 oxygen atoms and from 0 to 6 nitrogen atoms, and R^4 through R^9 are independently selected from among hydrogen and aliphatic groups containing 1 to 5 carbon atoms. Exemplary diepoxides include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane, bis (3,4-epoxy-6-methylcyclohexylmethyl adipate), 2-(3,4-epoxycyclohexyl)-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane. The concentration of the acid scavenger in the fluid composition is preferably between about 1.5% and about 10%, more preferably between about 2% and about 8% by weight, which is generally sufficient to maintain the hydraulic fluid in a serviceable condition for up to approximately 3000 hours of aircraft operation.

To limit the effect of temperature on viscosity, the composition further includes a polymeric viscosity index improver. Preferably, the viscosity index improver comprises a poly(alkyl methacrylate) ester of the type described in U.S. Pat. No. 3,718,596. Generally, the viscosity index improver is of high molecular weight, having a number average molecular weight of between about 50,000 and about 100,000 and a weight average molecular weight of between about 200,000 and about 300,000. Preferably, the viscosity index improver of the invention has a relatively narrow range of molecular weight, approximately 95% by weight of the viscosity index improver component having a molecular weight of between about 50,000 and about 1,500,000. This result is achieved in part by utilization of predominantly butyl and hexyl methacrylate esters. The viscosity index improver is present in a proportion sufficient to impart a kinematic viscosity of: at least about 3.0, preferably between about 3 and about 5 centistokes at 210° F.; at least about 9, preferably between about 9 and about 15 centistokes at 100° F.; and not more than about 4200 centistokes at −65° F. Superior shear stability characteristics are also imparted by the viscosity index improver used in the composition. Preferably the fluid composition contains between about 3% and about 10% by weight of the viscosity index improver. Nonlimiting particularly preferred viscosity index improvers are those sold under the trade designations PA6703, PA6477, and PA6961-PMN by Rohm and Haas Company. The viscosity index improver, as previously noted in the Summary of the Invention, is conveniently provided in the form of a solution in a phosphate ester solvent, preferably a trialkyl phosphate ester such as tributyl or triisobutyl phosphate, or a combination of alkyl and phenyl derivatives. The proportions referred to above for the viscosity index improver are on a solids (methacrylate polymer) basis. The phosphate ester solvent becomes in effect part of the base stock, and the ranges of proportions of phosphate esters, as discussed above, reflect the phosphate ester added as a vehicle for the viscosity index improver.

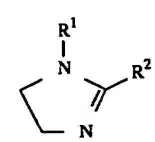
An anti-erosion agent is incorporated in an amount effective to inhibit flow-induced electrochemical corrosion, more

precisely referred to as zeta corrosion. The anti-erosion additive is preferably an alkali metal salt, more preferably a potassium salt of a perfluoroalkylsulfonic acid. Such anti-erosion additives are more fully described in U.S. Pat. No. 3,679,587. Typically, the alkyl component comprises hexyl, heptyl, octyl, nonyl, decyl, or mixtures thereof, with perfluorooctyl generally affording the best properties. It is particularly preferred that the anti-erosion agent predominantly comprises the potassium salt of perfluorooctylsulfonic acid in a proportion of between about 250 and about 1000 most preferably at least about 500 ppm. In the operation of an aircraft hydraulic fluid system, the sulfonic acid moiety of the anti-erosion agent tends to lower the surface tension of the hydraulic fluid and thereby better cover the metal surfaces with which the hydraulic fluid normally comes in contact. The metering edges of servo valves are generally the most important metal parts which need protection from electrochemical corrosion. Positive ions in the fluid, including the alkali metal ion of the anti-erosion agent, are adsorbed onto the metal surface and neutralize the negative charges on the metal that are otherwise created by the rapid flow of the hydraulic fluid over the servo valve metering edges. Enhanced erosion resistance is provided in the composition of the invention, which preferably contains a perfluoroalkylsulfonic salt content about twice that of the prior art composition sold as LD4.

Limiting the diaryl ester content of the base stock contributes to thermal, oxidative, and hydrolytic stability of the fluid. The composition of the invention also contains a combination of antioxidant additives, preferably including both a hindered phenol and a hindered polyphenol. Hydrolytic stability has been found to be improved by partially substituting the hindered polyphenol for the phenol, and it is thus preferred that the composition contain not more than about 1.0%, preferably not more than about 0.7% by weight of a phenol such as a 2,4,6-trialkylphenol. It is generally preferred that the composition contain between about 0.1% and about 0.7% of a 2,4,6-trialkylphenol, preferably 2,6-ditertiary-butyl-p-cresol [also written as 2,6-di-tert-butyl-p-cresol or 2,6-di-t-butyl-p-cresol ("Ionol")]. The composition should further include between about 0.3% and about 1% of a hindered polyphenol compound, such as a bis(3,5-dialkyl-4-hydroxyaryl) methane, for example, the bis(3,5-di-tert-butyl-4-hydroxyphenyl)methane sold under the trade designation Ethanox® 702 by the Ethyl Corp., a 1,3,5-trialkyl-2,4,6-tris(3,5 -dialkyl-4-hydroxyaryl) aromatic compound, for example, the 1,3,5-trimethyl-2,4,6 -tris(3,5-di-tert-butyl-4-hydroxyphenyl)benzene sold under the trade designation Ethanox® 330 by the Ethyl Corp., or mixtures thereof. The composition may also include an amine antioxidant, preferably a diarylamine such as, for example, phenyl-α-napthylamine or alkylphenyl-α-naphthylamine, or the reaction product of N-phenylbenzylamine with 2,4,4-trimethylpentene sold under the trade designation Irganox® L-57 by Ciba-Geigy; diphenylamine, ditolylamine, phenyl tolylamine, 4,4'-diaminodiphenylamine, di-p-methoxydiphenylamine, or 4-cyclohexylaminodiphenylamine; a carbazole compound such as N-methylcarbazole, N-ethylcarbazole, or 3-hydroxycarbazole; an aminophenol such a N-butylaminophenol, N-methyl-N-amylaminophenol, or N-isooctyl-p-amino-phenol; an aminodiphenylalkane such as aminodiphenylmethanes, 4,4'-diaminodiphenylmethane, etc., aminodiphenylethers; aminodiphenyl thioethers; aryl substituted alkylenediamines such as 1,2-di-o-toluidoethane, 1,2-dianilinoethane, or 1,2-dianilinopropane; aminobiphenyls, such as 5-hydroxy-2-aminobiphenyl, etc.; the reaction product of an aldehyde or ketone with an amine such as the reaction product of acetone and diphenylamine; the reaction product of a complex diarylamine and a ketone or aldehyde; a morpholine such as N-(p-hydroxyphenyl)morpholine, etc.; an amidine such as N,N'-bis-(hydroxyphenyl)acetamidine or the like; an acridan such as 9,9'-dimethylacridan, a phenathiazine such as phenathiazine, 3,7-dibutylphenathiazine or 6,6-dioctylphenathiazine; a cyclohexylamine; or mixtures thereof. An alkyl substituted diphenylamine such as di(p-octylphenyl) amine is preferred. Certain amine components can also act as a lubricating additive. The amine antioxidant is also preferably present in a proportion of between about 0.3 and about 1% by weight. By maintaining the Ionol content of the fluid composition below 1.0%, preferably below 0.7%, and more preferably below 0.5% by weight,-toxicity of the composition is even lower than that of Skydrol® LD-4 hydraulic fluid.

As a copper corrosion inhibitor, the composition of the invention preferably includes a benzotriazole derivative, such as that sold under the trade designation Petrolite 57068. This corrosion inhibitor is present in an amount sufficient to deactivate metal surfaces in contact with the fluid composition against the formation of metal oxides on the metal surfaces in contact with the fluid, thereby reducing rates of copper dissolution into the hydraulic fluid, and also reducing dissolution of perhaps parts fabricated from copper alloys. Advantageously, the composition contains between about 0.005% and about 0.09% by weight of the benzotriazole derivative, preferably between about 0.02 and about 0.07% by weight.

Phosphate ester functional fluids are known to corrode iron alloys as well as copper alloys. Numerous iron corrosion inhibitors are available for use in functional fluids, but these are known in many instances to increase rates of erosion and thus have a net deleterious effect on the performance properties of the hydraulic fluid. However, in accordance with the invention, it has been discovered that certain 4,5-dihydroimidazole compounds are effective iron corrosion inhibitors, yet do not adversely affect the erosion properties of the fluid. Useful 4,5-dihydroimidazole compounds include those which correspond to the structural formula



where R^1 is hydrogen, alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl, alkoxyalkyl or alkoxyalkenyl, and R^2 is alkyl, alkenyl or an aliphatic carboxylate. Exemplary groups which may constitute R^1 include hydrogen, methyl, ethyl, propyl, butyl, pentyl, octyl, vinyl, propenyl, octenyl, hexenyl, hydroxyethyl, hydroxyhexyl, methoxypropyl, propoxyethyl, butoxypropenyl, etc. Exemplary group, which may constitute R^2 include, octyl, dodecyl, hexadecyl, heptadecenyl, or a fatty acid substituent such as 8-carboxyoctyl, 12-carboxydodecyl, 16-carboxyhexadecenyl, or 18-carboxyoctadecyl. In a particularly effective embodiment, R^1 is hydrogen or lower alkyl and R^2 is a fatty acid residue containing at least about 9 carbon atoms, i.e., —C_8—COOH to —C_{18} COOH, preferably C_{16}—C_{18}—COOH. In another preferred embodiment, R^1 is a lower hydroxyalkyl and R^2 is a C_8—C_{18} alkenyl. In the latter instance, however, the most satisfactory inhibition of Fe corrosion is realized only if the 4,5-dihydro-imidazole is used in combination with an amino acid derivative, more particularly an N-substituted amino

acid in which the N-substituent contains both polar and oleophilic moieties, for example, an N-alkyl-N-oxo-alkenyl amino acid.

It has further and unexpectedly been discovered that the presence of such a 4,5-dihydroimidazole compound, typically in a proportion of between about 0.01% and about 0.1% by weight, not only inhibits iron corrosion but contributes markedly to the stability of the functional fluid as indicated by epoxide depletion.

It has been found that the salutary effect of the 4,5-dihydroimidazole compound is enhanced if it is used in combination with a phenolic antioxidant, especially a complex hindered polyphenol such as a bis(3,5-dialkyl-4-hydroxyaryl)methane or a 1,3,5-trialkyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxyaryl)benzene. Exemplary of such complex hindered polyphenol compounds, respectively, are bis(3,5-di-tert-butyl-4-hydroxyphenyl)methane and 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenyl)benzene. Optimal effect on stability has been observed using a combination of the condensation product of 4,5-dihydro-1H-imidazole and C_{16}–C_{18} fatty acid (sold under the trade designation Vanlube RI-G by the Vanderbilt Co.) with a hindered polyphenol and an alkyl substituted diarylamine such as di(p-octylphenyl)amine. Also effective as a 4,5-dihydroimidazole compound in such combination is 2-(8-heptadecenyl)-4,5-dihydro-1H-imidazole-1-ethanol (sold under the trade designation Amine-O by Ciba-Geigy) To function as an iron corrosion inhibitor, the latter compound should be used in combination with an amino acid derivative such as, e.g., the N-methyl-N-(1-oxo-9-octadecenyl)glycine sold under the trade designation Sarkosyl®-O by Ciba-Geigy Corporation.

It has been found that a still further enhancement in high temperature stability is realized where the 4,5-dihydroimidazole compound is used in combination with a phosphate ester base stock in which the alkyl substituents attached to the phosphate moiety are substantially isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl).

Although they have not been found to produce the substantial advantageous effect on high temperature stability that is afforded by the use of an a 4,5-dihydroimidazole compound, other iron corrosion inhibitors have been found effective in the functional fluid of the invention without adverse effect on erosion characteristics. Acceptable iron corrosion inhibitors include, for example, the product sold by Petrolite under the trade designation Petrolite P-31001.

As necessary, the fluid composition may also contain an anti-foaming agent. Preferably, this is a silicone fluid, more preferably a polyalkylsiloxane, for example, the polymethylsiloxane sold under the trade designation DC 200 by Dow Corning. Preferably the anti-foam agent is included in a proportion sufficient to inhibit foam formation under the test conditions of ASTM method 892. Typically, the anti-foam content of the composition is at least about 0.0005% by weight, typically about 0.0001% to about 0.001% by weight.

Preferably, the pH of the composition of the invention is at least about 7.5, more preferably between about 7.5 and about 9.0. To impart a pH in this range and to enhance the acid scavenging capacity of the formulation, the composition may further include between about 0.0035 and about 0.10%, preferably between about 0.01% and about 0.1% by weight, most preferably between about 0.02% and about 0.07% of an alkali metal phenate or other arenate. Potassium phenate is preferred. In addition to neutralizing acidic components of the composition, the alkali metal arenate serves to pacify the metal surfaces when the composition has been added to a hydraulic system, thereby reducing corrosion.

Although optimal properties are realized in a composition of low alkyl diaryl phosphate content and particularly in compositions using the base stock of the invention as described above, the additive combination of the invention also affords beneficial results when used in combination with any of a variety of base stock compositions known to the art. The benefit of using esters whose alkyl substituents are predominantly comprised of isoalkyl C_4 or C_5 (namely isobutyl or isopentyl) also extends beyond the preferred concentration ranges outlined above. Broadly, the additive combination can be used with an organophosphate ester base stock comprising between about 10% and about 100%, preferably between about 10% and about 99%, by weight of a trialkyl phosphate wherein the alkyl substituents are substantially C_4 or C_5 (namely, butyl or pentyl), preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), between about 0% and about 70% by weight of a dialkyl aryl phosphate wherein the alkyl substituents are substantially C_4 or C_5 (namely, butyl or pentyl), preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), and between about 0% and about 25% by weight of an alkyl diaryl phosphate wherein the alkyl substituents are substantially C_4 or C_5 (namely, butyl or pentyl), preferably isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl). In a preferred embodiment, the additive combination is used with a base stock comprising between about 10% and about 100%, preferably between about 35% and about 99%, by weight of a tributyl or tripentyl phosphate, more preferably triisobutyl or triisopentyl phosphate, between about 0% and about 35% by weight of a dibutyl aryl or dipentyl aryl phosphate, more preferably diisobutyl aryl or diisopentyl aryl phosphate, and between about 0% and about 20% by weight of a triaryl phosphate, and between about 0% and about 20% by weight of a triaryl phosphate. The additive combination is also effective in combination with other ranges of base stock compositions as set forth below:

TABLE 1

Phosphate Ester	Base Stock, Weight % I	II	III	IV	V
Tri (C_4/C_5 alkyl)[1]	10–72	10–25	50–72	80–99	50–72
Di(C_4/C_5 alkyl)[1] Aryl	18–70	45–70	18–75		18–75
C_4/C_5 Alkyl[1] Diaryl	0–25	5–25	0–10		0–10
Triaryl				1–20	0–10

[1]In a preferred embodiment, the alkyl substituents are isoalkyl C_4 or C_5.

As discussed hereinabove, optimal properties are achieved by combining the preferred isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl) phosphate ester base stock with the additive combination of the invention. However, significant benefits in lower toxicity, lower density, hydrolytic stability, oxidative stability, and thermal stability are afforded by the use of the isoalkyl esters with other additive combinations as well, while, at the same time, maintaining a level of seal integrity equivalent to that experienced by the corresponding normal alkyl phosphate esters. In a preferred embodiment, the isoalkyl C_4 or C_5 phosphate ester base stock contains between about 10% and 100%, preferably between about 50% and about 85%, by weight of a trialkyl phosphate wherein the alkyl substituents are substantially isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), between about 18% and about 35% by weight of a dialkyl aryl phosphate wherein the alkyl substituents are substantially isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl), and between about 0% and about 10% by weight, preferably between about 0% and about 5% by weight, of an alkyl

diaryl phosphate wherein the alkyl substituents are substantially isoalkyl C_4 or C_5 (namely, isobutyl or isopentyl). However, the benefits of using the isoalkyl substituents are so substantial that they are realized to a significant extent over a considerably broader range of composition. Generally, therefore, a base stock which utilizes isoalkyl esters may comprise 100%, preferably between about 10% and about 90%, by weight of a triisobutyl or triisopentyl phosphate, between about 0% and about 70% by weight of a diisobutyl or diisopentyl aryl phosphate and between about 0% and about 25% by weight of an alkyl diaryl phosphate. Preferably, the alkyl substituent of the alkyl diaryl phosphate is also isobutyl or isopentyl, especially when the alkyl diaryl phosphate content exceeds about 5%. The aryl substituents of these esters are typically phenyl, but may also be an alkyl-substituted phenyl (alkylphenyl) wherein the alkyl substituent is C_1 to C_9, preferably C_3 to C_4. Nonlimiting examples of the alkyl-substituted phenyl substituents include tolyl (also known as methylphenyl), ethylphenyl, isopropylphenyl, isobutylphenyl, tert-butylphenyl, and the like.

The isoalkyl base stock should be combined with an acid scavenger in an amount effective to neutralize phosphoric acid or phosphoric acid partial esters formed in situ by hydrolysis of any of the phosphate esters of the base stock. The acid scavengers described above are preferred but other acid scavengers known to the art may be used. The isoalkyl based functional fluids should also contain an antierosion additive in an amount effective to inhibit flow induced electrochemical corrosion of flow metering edges of hydraulic servo valves in hydraulic systems. These fluids should also contain a viscosity index improver in an amount effective to cause the fluid composition to exhibit the viscosity index stated above. The composition should further include an antioxidant in an amount effective to inhibit oxidation of the fluid composition components in the presence of oxidizing agents. Preferably, the anti-erosion agent, viscosity index improver, and antioxidant composition are as described above, but the benefits of the use of an isoalkyl base stock are also realized with other additive combinations known to the art.

Methods known to those skilled in the art may be used for the preparation of the compositions of the invention. For example, a base stock comprising the phosphate esters may be prepared by mixing in an agitated stainless steel vessel. Additives may then be blended into the base stock in the same vessel. As noted above, the viscosity index improver is preferably added in the form of a solution in a phosphate ester solvent.

At temperatures above 200° F., the more preferred functional fluid compositions of the invention exhibit thermal, oxidative, and hydrolytic stability two to three times greater than that of Skydrol® LD-4 hydraulic fluid as measured by the depletion of epoxide acid scavenger as a function of time. Superior stability is exhibited even in the presence of halogen-containing compounds such as trichloroethane. When a 4,5-dihydroimidazole compound is included, the extent of improvement is even greater. As a result of the relatively low phenyl ester content, the composition of the invention has a density of less than one gram per cc, typically between about 0.97 and about 0.99 grams per cc. This is a desirable feature from the standpoint of fuel burn (consumption) in aircraft.

Shear stability of the fluid composition also compares favorably with commercially available aircraft hydraulic fluids. Thus, for example, after 500 hour exposure to an accelerated degradation test in a typical aircraft hydraulic pump system, the viscosity of the composition at −65° drops only from 4000 to 2400. In part, this advantage is believed to result from the narrower range of molecular weight of the viscosity index improver. Exposure to shear conditions tends to degrade higher molecular weight viscosity index improvers, so that compositions in which the molecular weight of the viscosity index improver is distributed over a broad range tend to suffer a greater loss of effectiveness over time due to breakdown of the higher molecular weight species.

In part due to the relatively low concentration of 2,6-di-tert-butyl-p-cresol, the toxicity of the fluid composition in the invention is very low. Where an isoalkyl ester base stock is used, toxicity is even lower.

The following examples illustrate the invention.

EXAMPLE 1

A hydraulic fluid having the composition set forth in Table 1 was prepared by mixing at ambient temperature in a 50 gallon stainless steel tank agitated with a 25 horsepower agitator having an anchor type impeller. The phosphate ester components were introduced into the tank first and, after a 30 minute period of initial mixing, the other additives were added in the sequence indicated in Table 2.

TABLE 2

Component	Basis: 100 Gram Batch Grams	Basis: 80 Gallon Batch Grams / Pounds
Tributyl Phosphate, Neat	49.0135	148,216.8 / 326.8
Dibutyl Phenyl Phosphate Of Low Diphenyl Content (Less Than 2% By Weight)	26.34	79,652.2 / 175.6 DRUM 2(~220#)
Methacrylate Ester Viscosity Index Improver (PA6477, 45.3% solids in 54.7% tributyl phosphate)	16.56	50,077 / 110.4 22684.9 gSLDS
3,4 Epoxycyclohexane Carboxylate	6.3	19,051 / 42
Potassium Perfluoroctylsulfonate (FC98)	.05	151.2 /
Benzotriazole type Copper Corrosion Inhibitor (P57068,Petrolite (50% Active), EX1663	.05	151.2 /
Iron Corrosion Inhibitor (90-31001,Petrolite (50% Active)	.05	151.2 /
Dye	.001	3.024 /
Potassium Phenate	.035	105.84 /
Di(p-octylphenyl)amine	0.45	1,361 / 3
2,6-Di-tert-butyl-p-cresol	0.25	756 / 1.667
Antifoam (Dow-Corning)	0.0005	1.512 /

This composition had a density of 0.996 g/cc at a temperature of 25° C. Of the source of dibutyl phenyl phosphate, 77.135% by weight was dibutyl phenyl phosphate or butyl diphenyl phosphate, so that 20.3% by weight of the overall composition was constituted of phosphate esters containing a phenyl moiety. However, the butyl diphenyl phosphate content was less than 1% by weight. Triphenyl phosphate content was essentially nil.

EXAMPLE 2

A second aircraft hydraulic fluid composition was prepared in the manner generally described in Example 1. The

composition of this fluid is set forth in Table 3.

TABLE 3

Density of Variables	Basis: 100 Gram Batch Grams	Basis: 80 Gallon Batch Grams / Pounds
Tributyl Phosphate	50.5988	152,999.3 / 337.3
Dibutyl Phenyl Phosphate Of Low Diphenyl Content (Less Than 2% By Weight)	24.0947	72,862.3 / 106.63
Methacrylate Ester Viscosity Index Improver (PA6477, 43.8% solids/56.2% tributyl phosphate)		22,684.9 gSLDS Total
3,4 Epoxycyclohexane Carboxylate	6.3	19,051 / 42
Potassium Perfluorooctylsulfonate (FC98)	.05	151.2 /
Benzotriazole Type Copper Corrosion Inhibitor (P57068,Petrolite; 50% Active)	.05	151.2 /
Iron Corrosion Inhibitor (90-31001,Petrolite (50% Active), EXI663	.05	151.2 /
Dye	.001	3.024 /
Potassium Phenate	.035	105.84 /
Di(p-octylphenyl)amine	.45	1,361 / 3
Dow Corning Anti-Foam	.0005	1.512 /
2,6-Di-tert-butyl-p-cresol	.25	756 / 1,667

This composition also exhibited a density of 0.996 g/cc at a temperature of 25° C. Of the source of dibutyl phenyl phosphate, 84.751% by weight was constituted of esters which contained no phenyl moiety. The overall composition contained 20.3% by weight of phosphate esters having a phenyl moiety, but less than 1% by weight butyl diphenyl phosphate and essentially no triphenyl phosphate.

Set forth in Table 4 are a partial elemental analysis and measured physical properties of the compositions of Examples 1 and 2. These data establish that the fluid composition of Examples 1 and 2 meet or exceed the airframe manufacturers' specification, for properties needed to qualify a product for use as an aircraft hydraulic fluid.

TABLE 4

	BATCH 1	BATCH 2
COLOR	PASS	PASS
CHLORINE, PPM	20	21
K+	106	99
S	57	83
Ca	<1	<1
Na	1.4	1.5
SP. G.	.9972	.9975
VISC. 210 F, CST	4.75	4.81
100	13.65	13.91
−65	1635	1628
MOISTURE	.10	.12
NEUT NO	.01	.02
POUR PT. °F.	<−80	<−80
AIT,F	850	920
FLASH PT.	350	360
FIRE PT.	360	390
CONDUCTIVITY	.65	.55
OXIRANE NO.	.39	.40
FOAM SEQ 1	170/65	180/20
2	30/10	40/44

TABLE 4-continued

	BATCH 1	BATCH 2
3	80/35	140/56
PARTICLE COUNT 5–15	7247	3116
15–25	1444	513
25–50	460	180
50–100	75	53
>100	14	10
SILTING INDEX	1.18	1.05

EXAMPLE 3

Tests were conducted comparing the thermal, oxidative and hydrolytic stability of the hydraulic fluid compositions of Examples 1 and 2 with commercially available hydraulic fluids. In each of these tests, a 301 stainless steel tube was filled to 80% capacity with the fluid to be tested. The temperature was maintained constant in each test. Comparative tests were run at 50° F. and 275° F., and further tests of the composition of the invention were run at 300° F. In all tests, five corrosion coupons were immersed in the fluid.

In some of the tests, the head space in the tube was filled with air, in others it was filled with nitrogen. After each tube was filled with the appropriate test composition, it was capped and heated to a predetermined test temperature and maintained at that temperature so that hydrolytic stability at such temperature could be determined. Each tube was monitored over time and samples were taken to follow trends in the fluid's chemical composition, in particular the concentration of the acid scavenger (epoxide) present in the sample. When the epoxide is 100% depleted, the fluid is typically degraded to the point that its usefulness as an aircraft hydraulic fluid has essentially been exhausted. As epoxide depletion approached 100%, test specimens were titrated for acidity. When the neutralization number of the fluid reached 1.5 or greater, the test was halted.

Illustrated in FIGS. 1 to 3 are epoxide depletion curves for the compositions of the invention as compared to previously available aircraft hydraulic fluids. In these curves, and in those relating to the further examples set forth below, the legends "W17" and "W17R" designate a composition of Table 1 or 2 above. "2495B1" refers specifically to the composition of Table 1, and "2495B2" to the composition of Table 2. "H4A" refers to commercial hydraulic fluid sold by Chevron under the trade designation "Hyjet IVA®." "Epox A" means that the test was run with air in the head space of the stainless steel tube, so that the test specimen was exposed to thermal, hydrolytic, and oxidative effects. "Epox T" means that the head space contained nitrogen, so that the test primarily measured thermal hydrolytic effects only.

EXAMPLE 4

Further thermal, hydrolytic, and oxidative stability tests were conducted on the compositions of Example 1 and 2. These tests were carried out generally in the manner described in Example 3, except that 0.5% moisture was incorporated in the test samples to determine the effect of moisture on thermal stability. Test temperatures were 250° F. and 275° F. The results of these tests are plotted in FIGS. 4 and 5.

EXAMPLE 5

Additional thermal, oxidative, and hydrolytic stability tests comparing the compositions of the invention with those

previously available in the art were conducted in sealed pyrex tubes. In certain of the tests, corrosion coupons were immersed in the liquid contained in the pyrex tube. Except for the use of pyrex rather than stainless steel tubes, the tests were conducted in essentially the manner described in Example 3. Both the compositions of the invention and comparative fluids were tested at 300° F. in the presence of 0.1 to 0.5% moisture with five corrosion coupons immersed in the test samples. The results of these tests are set forth in FIGS. **6** to **8**. Additional tests on the compositions of the invention were conducted at 375° F. without moisture addition. The results of these tests are set forth in FIG. **9**.

EXAMPLE 6

Further thermal, oxidative, and hydrolytic stability tests were conducted generally in the manner described in Example 3, except that trichloroethane was added, in varying amounts, to the test specimens in order to determine the effect on stability. Test temperatures were 275° F. and 300° F. The results of the tests of this example are set forth in FIGS. **10** and **11**.

EXAMPLE 7

The oxidation and corrosion resistance of the fluid compositions of Examples 1 and 2 was compared with that of previously available aircraft hydraulic fluids by testing in accordance with federal test method FTM5308.7 This test severely stresses the fluid with regard to oxidation stability.

In each test the fluid was charged to a glass tube and tested in accordance with FTM 5308.7. The fluid was heated to a fixed temperature of 350° F. after which dried air was purged through the test fluid at a rate of 5 liters per hour. Samples were taken every 24 hours, or more frequently, and the test was halted when the neutralization number of the fluid reached 1.5 or greater. The results of the tests in this Example are illustrated in FIG. **12**.

EXAMPLE 8

Because erosion is a form of electrochemical corrosion, erosion characteristics of a hydraulic fluid composition can be measured by wall currents obtained during flow of the fluid through small simulated orifices similar to those in a test servo valve. Using a standard erosion test apparatus, tests were conducted comparing the erosion properties of the compositions of Examples 1 and 2 with aircraft hydraulic fluid compositions previously available to the art. In this test system, favorable erosion properties were indicated by low wall currents and the most favorable characteristics are indicated by a negative wall current. Set forth in Table 5 is a summary of the data obtained in testing the compositions of the invention and those previously available commercially.

Further erosion tests were conducted on various functional fluid compositions after storage in glass containers at contact with air at 225° F. Set forth in Table 6 are the results of these tests for samples stored for the indicated number of hours.

In these tables, two measurements are reported for conductivity of the specimen, one taken by applicant's assignee and the other by an outside testing laboratory. I_w designates wall current, i_t designates threshold current, and R_v is the rate of erosion. R_v is related to I_w and i_t by the function:

$$R_v=150I_w-18i_t$$

In Tables 5 and 6, the term: "LD4" refers to the product sold under the trademark "Skydrol® LD-4" by Monsanto; "SKY500B" and "B4" refer to another functional fluid product available from Monsanto under the trade designation "Skydrol® 500B4"; "LD5" refers to the composition of the invention; "FC_{96}" refers to an antierosion agent comprising a potassium salt of perfluorohexylsulfonic acid; "Ca+2" refers to the presence of Ca^{+2} di(perfluoromethylsulfonate) in a tested fluid; "AO" means that an antioxidant was present, typically a combination of Ionol and a hindered polyphenol such as bis(3,5-di-t-butylhydroxyphenyl-)methane; "X1" with reference to the antierosion agent in LD-4 means that the antierosion agent FC_{98} is present in the standard commercial concentration; "X2" and "X3" mean that the FC_{98} concentration has been doubled or tripled; "TBP" refers to tributyl phosphate; "DBPP" refers to dibutyl phenyl phosphate; "TEHP" refers to triethylhexyl phosphate; "Si—HC" refers to a tetraalkyl silane composition; "HT" is used to designate Skydrol® HT, a functional fluid formulation that has been sold by applicant's assignee; "TiBP" refers to triisobutyl phosphate; "FC98" refers to an antierosion agent comprising a potassium salt of perfluorooctylsulfonic acid; "EXI 663" refers to a benzotriazole Cu corrosion inhibitor; 31001 refers to a Petrolite Fe corrosion inhibitor; HALS refers to a hindered amine light stabilizer; "H4A" refers to various samples of the functional fluid sold commercially by Chevron under the trade designation Hyjet IVA; "W6", "W7", "W8," etc. refer to the compositions of the invention; "ERT" means the specimen had been used in Erosion Resistance Tests; and "ECT" means the specimen had been used in Erosion Control Tests.

TABLE 5

	EROSION TEST DATA SUMMARY				
Sample ID	Independent Lab Cond. μMHO/cm	MCC Cond μMHO/cm	I_w μA	I_t μA/cm²	R_v cm³/min/h
LD4,Duplicate8/88	0.370	0.410	0.036	2.650	−42.000
LD4	0.360	0.350	0.046	1.200	−15.000
LD4,W/FC98X2	0.640	0.620	0.012	6.000	−106.000
LD4[FC96.250 PPM]	0.240	0.320	0.110	0.310	11.000
LD4[FC96.1250 PPM]	0.780	0.810	0.089	2.350	−28.000
LD4[FC96.2500 PPM]	1.200	1.220	0.061	4.100	−65.000
LD4[FC98,73PPM]	0.190	0.240	0.086	0.700	0.000
LD4[500 PPM,Ca + 2.]	0.670	0.750	−0.005	13.000	−235.000
LD4[1000 PPMCa + 2.]	0.980	0.940	−0.003	<18.000	NEG
LD4[1500PPM,Ca + 2.]	1.200	1.150	−0.003	<19.000	NEG
HY JET IV	1.000		−0.034	1.850	−40.000
B4[500B4]	0.300		0.019	1.150	−18.000

TABLE 5-continued

EROSION TEST DATA SUMMARY					
Sample ID	Independent Lab Cond. μMHO/cm	MCC Cond μMHO/cm	I_w μA	I_t μA/cm^2	R_v cm^3/min/h
TBP	0.008		0.450	0.038	67.000
DBPP	0.008		0.460	0.094	67.000
TEHP	0.001		0.021	—	<3
Si-HC	0.000		<0.0001	—	<.0015
HT,FC98	0.037	0.690	0.410	0.210	58.000
HT,FC98X1	0.630	1.020	0.000	2.850	−54.000
TiBP	0.001NV		0.127	0.007	20.000
LD5[FC98,250PPM]	0.150		0.071	1.250	−12.000
LD5[FC98,750PPM]	0.250		0.015	1.400	−23.000
LD5[FC98.250PPM] .02% H_2O	0.140		−0.017	−0.061	NEG
LD5[SAME].1% H_2O	0.150		−0.007	−0.375	NEG
LD5[SAME].2% H_2O	0.150		−0.055	−0.375	NEG
LD5[SAME].3% H_2O	0.160		−0.085	−0.400	NEG
LD4,.1% H_2O[.51%]	0.370		0.001	2.000	
LD4,.2% H_2O[.45%]	0.380		0.007	1.700	
LD4,.3% H_2O[.56%]	0.400		0.014	1.800	
H4A	0.930		0.096	16.450	−262.000
H4,Used	0.300		0.011	2.300	−40.000
LD4,Used	0.390		−0.053	0.990	−26.000
SKY500A	0.039		0.185	0.600	16.950
H4A#2,Used	0.450		0.010	3.400	−59.700
H4A#1,Used	0.510		0.010	2.800	−48.900
H4A#3,Used	0.670		0.020	2.400	−40.200
LD4,Ca[S03C4F9]2	0.570		−0.020	>11	−201.000
H4A#5,Used + C1	0.670		0.020	2.400	−40.000
H4A#5,Used @ 195H, NO C1	0.770		0.050	7.400	−126.000
H4A#5,Used + C1,500H	0.440		0.026	0.260	−1.000
W6,Fresh	0.620	0.630	0.150	1.600	−6.000
Used-600 h.	0.630	0.740	−0.021	1.600	−55.000
W7,Fresh	0.490	0.590	0.140	1.300	−2.000
Used-600 h.	0.610	0.760	−0.013	2.200	−42.000
W8,Fresh	0.580	0.560	0.167	0.580	0.140
Used-600 h.	0.880	0.760	0.004	2.250	−40.000
W9,Fresh	0.540	0.640	0.230	1.400	11.000
W10,Fresh	0.310	0.380	0.230	1.400	9.000
Used-600 h.	0.730	0.750	0.036	2.000	−31.000
W11,Fresh	0.500	0.580	0.240	1.080	17.000
W12,Fresh	0.560	0.590	0.160	3.200	−34.000
Used-600 h.	0.670	0.690	0.160	2.500	−18.000
W13,Fresh	0.670	0.690	0.160	2.500	−21.000
Used-600 h.	0.970	1.000	0.001	2.750	−48.000
W14,Fresh	0.52	0.55	0.17	9.10	−138.00
Used-600 h.	0.67	0.73	−0.01	1.75	−33.00
W15,Fresh	0.51	0.54	0.16	0.63	13.00
Used-600 h.	0.62	0.75	−0.02	1.60	−31.00
W15Fresh,Erosion Control	0.07	0.54	−0.01	1.75	−33.00
Used-600 h.	0.75				
W16,Fresh	0.670				
W17,Fresh,Abex + 200 PPM C1	0.580		0.180	1.200	8.500
Used-600 h.	0.560		−0.028	0.720	−17.000
Used,ERT	0.610		−0.016 LT.	.29 GT.	−8
Used,ECT	0.66		−0.04 LT.	.35 GT.	−13
LD4 + FC910	0.230		0.026	1.500	−23.000
LD4 + H4A-AO'S	0.350		0.032	0.920	−12.000
LD4 + HALS,NO-FC98	0.015		0.120	0.140	16.000
LD4 + HALS + FC98	0.410		0.071	0.490	0.200
LD5,W17,2X-FC98 ONLY	0.420		0.110	2.250	−24.000
NBP4419198					
+50PPM EXI663	0.430		0.100	1.060	−4.000
+250PPM EXI663	0.430		0.110	1.070	−3.000
+1000PPM EXI663	0.450		0.120	1.120	−3.000
+50PPM 31001	0.420		0.120	1.060	−1.000
+250PPM 31001	0.430		0.100	1.080	−4.000
+5-PPM KP	0.450		0.170	0.510	16.000
+350 KP	0.700		0.210	0.800	17.000
+500PPM DODPA	0.430		0.120	1.080	−1.000
+5000PPM DODPA	0.420		0.120	1.080	−1.000

TABLE 5-continued

	EROSION TEST DATA SUMMARY				
Sample ID	Independent Lab Cond. μMHO/cm	MCC Cond μMHO/cm	I_w μA	I_t μA/cm²	R_v cm³/min/h
LD5,W17,NO AEA	0.023		0.230 LT.	.01 GT.	34
NBP4419199 + 160 PPM $Ca(SO_3C4F9)_2$	0.31		−0.01 GT.	12 LT.	−220

TABLE 6

Erosion Test Data After Oven Heating 225 F, In Glass; Air @ Start Only; Includes 1020 Steel and Cu Corr. Coupons					
	Independent Lab Cond. μmHo/cm.	MCC Cond. μmHO/cm	I_w μA	I_t μA	Rv m3/min/h.
LD-4 Hours					
100.000	0.390		0.039	2.500	−39.000
200.00	0.410		−0.009	0.200	−5.000
300.00	0.410		−0.001	0.170	−4.000
600.00	0.360		0.012	0.410	−6.000
H4A Hours					
100.000	1.200		0.087	0.097	11.000
200.000	1.100		0.083	0.330	6.000
300.00	1.000		0.088	0.280	8.000
600.00	1.100		0.086	0.350	7.000

EXAMPLE 9

The compositions of Examples 1 and 2 were compared with an available commercial hydraulic fluid in a storage test at 375° F. in the presence of iron. After 21 hours storage at such conditions, analyses were made of the solids build-up in the fluid. More particularly, measurements were made of the build-up of metal solids, other solids, and total solids. The results of these tests are illustrated in FIG. 13.

EXAMPLE 10

Aircraft hydraulic fluids of the invention were formulated, substantially in the manner described in Example 1, and subjected to the Erosion Resistance Test of Boeing Material Specification for Fire Resistant Hydraulic Fluid, BMS 3-11G (Rev. Jul. 17, 1986). Set forth in Tables 7, 7A, and 7B are the compositions of the fluids tested. Set forth in Table 8 are the results of the erosion tests. Set forth in Tables 9 and 9A is a comparison of the properties of the fluids before and after subjection to the erosion tests. In these tables, "HF 400," "HF-411," and "HF-460" refer to poly(butyl/hexyl methacrylate) viscosity index improvers. In each entry, the table states the butyl methacrylate polymer solids content, the balance being trialkyl phosphate solvent. "AEA" refers to an antierosion agent, "PANA" designates phenyl-α-napthylamine; "APANA" designates an alkylphenyl-α-naphthylamine. "DODPA" refers to di(p-octylphenyl)amine; "P58526 Petrolite" is an iron corrosion inhibitor; "DC 200, 100 CST" is a Dow-Corning antifoam; "SARK O" refers to the N-methyl-N-1-OXO-9-octadenyl) glycine sold under the trade designation "Sarkosyl-O" by Ciba-Geigy; "AMINE O" refers to the 2-(8-heptadecenyl)-4,5-dihydro-1H-imidazole-1-ethanol sold under the trade designation "Amino-O" by Ciba-Geigy; "90-31001" refers to Petrolite 31001; and "FH-132" refers to diphenyldithioethane.

TABLE 7

	FORMULATIONS				
VARIABLE	W-1	W-2	W-3	W-4	W-5
TiBp	54.29[a]	53.33[a]	54.58[a]	52.61[a]	39.8653[a]
DiBPP,66.3% PH	29.90[b]	29.92[b]	29.90[b]	29.88[b]	26.45[b]
PA6385	8.52	8.47	8.21	—	—
PA6703	—	—	—	10.16	10.16
MCS 1562	6.3	6.3	6.3	6.3	6.3
AEA,FC98	.05	.05	.05	.05	.05
P57068,PET.(50% ACTIVE)	.05	.05	.05	.05	.05
DYE	.00	.001	.001	.001	.001
KP	.03	.035	.035	.035	.035
E702	.90	—	.45	.45	.9
DODPA	.45	.45	.15	.45	.45
IONOL	.25	—	.25	.25	.25
DC 200,100CST	.005	.0005	.0005	.0005	.0005
VANLUBE RI-G	—	—	.025	.025	0.025
L130	1.	—	—	—	—
E330	.3	1.05	—	—	—
L57	.4	—	—	—	—
E703	.3	.35	—	—	—

TABLE 7-continued

[a]Triisobutyl phosphate
[b]Diisobutyl phenyl phosphate

VARIABLE	FORMULATIONS W15A	W17	W18
TBP	39.8653	49.3685	39.8653
DBPP,LOW DI-PHENYL,ROD/C2	35.76 (D56.8P)	26.45	26.45
DBPP,LOW DI-PHENYL,ROD/C4			
HF400,43.6%S/7.5%FINAL	17.36	17.36	
HF411,35.5%s/3.75%FINAL	6.41		
HF460,58.5%s/3.75%FINAL	10.42		
MCS 1562	5.8	6.3	6.3
AEA,FC98	.05	.05	.05
P57068,PETROLITE (50% ACTIVE)	.04	.05	.05
EXI-663			
DYE	.001	.001	.001
KP	.035	.035	.035
E702	.76	.9	.9
DODPA	.	.45	.45
IONOL	.	.25	.25
A-PANA	.85	.	.
P58528,PETROLITE (50% ACTIVE)	.	.05	.05
90-31001			
DC 200,100 CST	.0005	.0005	.0005
SARK O	.004	.	.
AMINE O	.004	.	.
FH132			.25

TABLE 7A

VARIABLES	FORMULATIONS W6	W7	W8
TBP,REDIST.	45.835	.	.
TBP	.	50.844	50.8935
DBPP,LOW DI-PHENYL,ROD/C2	30.	25.	25.
DBPP,LOW DI-PHENYL,ROD/C4	.	.	.
HF400,43.6%S/7.5%FINAL	.	.	.
HF411,35.5%S/3.75%FINAL	10.42	10.275	10.275
HF460,58.5%S/3.75%FINAL	6.41	6.41	6.41
MCS 1562	5.8	5.8	5.8
AEA,FC98	.05	.05	.05
P57068,PETROLITE (50% ACTIVE)	.055	.1	.1
DYE	.001	.001	.001
KP	.035	.035	.01
E702	.761	.	.
PANA	.625	.	.
APANA	.	.76	.9
DODPA	.	.625	.45
P58528,PETROLITE (50% ACTIVE)	.	.1	.1
DC 200,100 CST	.	.	.0005
SARK O	.004	.	.
AMINE O	.004	.	.
(1)KP,SELFMADE KP		-	
2% BDPP IN DBPP			

TABLE 7B

VARIABLES	FORMULATION W15
TBP	39.8653
DBPP, LOW DI-PHENYL,ROD/C2	35.76(D/56.8P)
DBPP, LOW DI-PHENYL,ROD/C4	
HF400,43.6%s/7.5%FINAL	
HF411,35.5%s/3.75%FINAL	6.41
HF460,58.5%s/3.75%FINAL	10.42
MCS 1562	5.8
AEA,FC98	.05
P57068,PETROLITE (50% ACTIVE)	.04
EXI-663	
DYE	.001
KP	.035
E702	E702.76
PANA	.85
P58528,PETROLITE (50% ACTIVE)	
90-31001	
DC 200,100 CST	.0005
SARK O	.004
AMINE O	.004

TABLE 8

RUN NUMBER	3	4	5	6	7	8
RIG USED	A	A	A	C	A	C
CASE DRAIN TEMPERATURE (°F.)	290	290	290	315	315	315
RESERVOIR TEMPERATURE	275	275	275	300	300	300
Cl ADDED, PPM	0	0	0	0	0	0
TOTAL RUN TIME, HR	468	368	570	560	475	420
OPERATING PROBLEMS	O rings	O rings	shut downs	none	pump water	pump water
BOEING VALVE DATA						
SLIDE AND SLEEVE NO.	W004	W004	W002	W011	W008	W011
PORT NUMBERS	5.7	6.8	6.8	1.3	1.3	2.4
FLOW INCREASE, cc/min.	erratic	erratic	erratic	40	200	200
ACCEPTABLE?	no	no	no	yes	marginal	marginal
EDGE APPEARANCE	slight wear	slight wear	slight wear	shaded	slight wear	slight wear
PUMP DATA						
MANUFACTURER	Vickers	Vickers	Vickers	Abex	Vickers	Abex
SERIAL NO.	491761	491761	491761	166495	482891	166495
HRS AT START	0	468	856	1000 @225 F.	0	1562
HRS TO FALURE	468	856	1426	no failure	476	1980
CAUSE OF FAILURE	O ring	O ring	bearings	—	bearings	bearings shaft seal
SECOND PUMP (IF USED)						
MFR						
S/N						
HRS AT START						
HRS TO FAILURE						

RUN NUMBER	15 ERT	15 ECT	17 ERT
RIG USED	C	A	C
CASE DRAIN TEMPERATURE (°F.)	315	275	300
RESERVOIR TEMPERATURE	300	280	284
Cl ADDED, PPM	1000	1000	200
TOTAL RUN TIME, HR	274	245	500
OPERATING PROBLEMS	none	none	shaft seal
BOEING VALVE DATA			
SLIDE AND SLEEVE NO.	W007	W022	W007
PORT NUMBERS	6.8	5.7	1.3
FLOW INCREASE, cc/min.	extreme	extreme	300
ACCEPTABLE?	no	no	marginal
EDGE APPEARANCE	severe wear	severe wear	slight shading
PUMP DATA			
MANUFACTURER	Abex	Vickers	Abex
SERIAL NO.	183629	491761	115815
HRS AT START	0	0	0
HRS TO FAILURE	274	230	320
CAUSE OF FAILURE	Ou transfer	Ou transfer	shaft seal
SECOND PUMP (IF USED)			
MFR		Vickers	Abex
S/N		491763	228188
HRS AT START		+ 492891 both destroyed	0
HRS TO FAILURE			130

RUN NUMBER	17 ERT	17 ECT	17 BASE CASE	17 AIRBUS	17 @225 F.	17 BMS PUMPING	18 ERT	18 BASE CASE
RIG USED	A	A	C	C	B	HP	B	A
CASE DRAIN TEMPERATURE (°F.)	300	275	300	290	240	284	300	300
RESERVOIR TEMPERATURE	284	260	284	273	225	235	284	284
Cl ADDED, PPM	200	400	0	0	1000	0	200	0
TOTAL RUN TIME, HR	500	330	800	1000	1000	500	500	760

TABLE 8-continued

OPERATING PROBLEMS	none	none	pump water	none	none	none	none	none
BOEING VALVE DATA								
SLIDE AND SLEEVE NO.	W006	W022	W020	W020	W017	not used	W017	W016
PORT NUMBERS	2.4	1.3	1.3	5.7	6.8	—	2.4	2.4
FLOW INCREASE, cc/min.	100	500	0	40	170	—	40	136
ACCEPTABLE?	yes	yes	yes	yes	yes	—	yes	yes
EDGE APPEARANCE	slight shading	worn	slight shading	slight wear	slight wear	—	slight wear	slight wear
PUMP DATA								
MANUFACTURER	Vickers	Vickers	Abex	Abex	Vickers	Abex	Vickers	Vickers
SERIAL NO.	491761	491763	183629	226153	492891	L-1976	491762	491761
HRS AT START	0	0	0	0	0	0	0	0
HRS TO FALURE	no failure	no failure	676	1000	no failure	no failure	no failure	no failure
CAUSE OF FAILURE	—	—	bearings	bearings	—	—	—	—
SECOND PUMP (IF USED)								
MFR			Abex					
S/N			116815					
HRS AT START			0					
HRS TO FAILURE			117					

TABLE 9

SOME DATA FROM THE ANAL. FLUIDS;

MCS2510-	W1,FR	W1,U	W2,FR	W2,U	W3,FR	W3,U	W4,FR	W4,U	W5,FR	W5,U(@500 HRS)
SP. GR.	.9868	.9925	.9877	.9890	.9896	.9845	.9902	.9898	.9892	.9905
VISC 210	3.65	2.54	3.69	2.19	3.32	2.19	4.2	4.28	2.99	2.49
100	11.47	9.05	11.94	7.24	10.47	6.93	12.97	8.46	8.99	7.96
−65	3954	5754	4963	3302	3632	2685	3893	2158	2317	2421
NN	.02	ND	.01	1.05	.01	.04	.03	1.86	.01	.09
% H2O	.12	.04	.13	.11	.08	.05	.11	.02	.15	.07
AIT	930	930	94	0930	940	920	960	950	930	940
FL. PT	330	265	310	290	315	300	350	350	335	319
FI. PT.	350	335	340	330	355	350	370	390	365	381
OX. OX.	TD	TD	.41	TD	.38	TD	.39	.14	.61	.36
COND.	.44	—	.28	.90	.45	.37	.36	1.63	.41	.43
-% EPOX	—	86.5	—	65.3	—	22.1	—	78.9	—	57.8
Cl	15	154	25	173	12	257	7	204	18	136
HRS	580	—	502	—	579	—	334	—	933	—
TEMP. F.	290/284	—	293/284	—	297/290	—	278/270	—	300/280	—
PUMP RIG	A	—	—	A	—	B	—	A	—	C
AEA FC98	2XSTD	—	2XSTD	—	2XSTD	—	2XSTD	—	2XSTD	—

ICAP DATA:	W1,FR	W1,U	W2,FR	W2,U	W3,FR	W3,U	W4,FR	W4,U	W5,FR	W5,U
Na	5.23	28.3	2.5	8.1	4.7	8.8	3.2	14.9	3.9	8.7
K	74.6	87.	71.1	64.3	91.1	49.4	104.5	94.6	110.3	34.9
S	58.4	56.8	58.3	59.1	61.5	73.	79.3	79.5	63.9	73.8
Cu	1.32	720	<.125	142.1	1.1	.8	<.13	1112	<.13	6.7
Fe	<.5	134.9	<.125	11.9	<.25	<.5	<.13	140.3	<.13	1.3
Mn	<.5	1.53	<.125	<.5	<.25	<.5	<.13	.86	<.13	<.5
Zn	<.5	93.9	<.125	14.28	<.25	<.5	<.13	131.	<.13	.9
Al	<.5	1.11	<.125	<.5	<.59	<.5	<.13	<.5	<.41	<.5
Cd	<.5	7.25	<.125	1.54	<.25	<.5	<.13	6.62	<.13	<.5
FOAM TEST (250/100)F (400/250U)	35/23	ND	ND	ND	ND	40/19	ND	160/91	80/34	50/21

	W6,FRESH	,-USED	W7,FRESH	,-USED	W8,FRESH	,-USED
SP. GR.	1.0015	1.0048	.9991	1.0003	.9993	.9995
VISC. 210	4.62	3.02	4.73	2.38	4.80	2.70
100	13.48	9.28	13.59	7.09	13.80	7.98
−65	1523	1181	1456	776	1471	809
NN	.02	1.09	.13	.14	.14	.212
% H2O	.07	.04	.11	.02	.16	.015
AIT	910	950	870	925	900	9700
FL. PT	320	315	320	300	330	3100
FI. PT.	360	365	360	350	375	3500
OX. OX.	.39	ND	.41	.14	.40	.118

TABLE 9-continued

COND.	.63	.74	.59	.76	.56	.768
-% EPOX	0	85.6	0	57.6	0	69.4
Cl	—	11	11	10	15	10
HRS	—	124/438	—	475	—	418
TEMP. F.	—	275/300	—	300	—	300
AEA,FC98		2XSTD	—	2X STD	2X STD	—
PUMP RIG	C	—	A−	—	C	—
O&C LIFE		72	—	120	—	120
SPAN @ 350 F., HRS						
ICAP DATA:	**W6/F**	**/U;**	**W7/F**	**/U;**	**W8/F**	**/U**
Na	<.5	2.58	<.5	2.07	<.5	3.1
K	112.7	54.95	98.06	83.54	72.58	49.15
S	96.53	103.2	94.97	144.5	81.94	75.17
Cu	<.5	1.13	<.5	23.5	<.5	3.37
Fe	<.5	<.5	<.5	<.5	<.5	1.63
Zn	<.5	1.42	<.5	6.96	<.5	17.94
Al	1.17	1.11	<.54	<.5	<.5	<.5
Cd	<.5	<.5	<.5	.54	<.5	<.5
FOAM TEST (250/100)F	500/1500,	35/15;	320/>600,	20/6	;180/83,	60/19
~INCR. IN INT. LEAKAGE CC'S/MIN	350 − 300 = 50		600 − 410 = 190		600 − 300 = 300	
) HR-RUN END 200< <500 HRS,	350 − 320 = 30		600 − 390 = 210		600 − 500 = 100	
EROSION TYPE	DE-ALLOYED		DE-ALLOYED		DE-ALLOYED	
VIA;SEM	X		ND		ND	
;VISUAL	X		X		X	
EROSIVE,PUMP	—	NO	—	YES(1)	—	YES(1)
,BECK	NO	NO	NO	NO	YES	NO

(1)LESS EROSION THAN H4A AT 225 F. FOR 600 HRS.

SOME DATA FROM THE ANAL. FLUIDS;

	W15 FRESH	USED ECT	USED ERT	W17 FRESH	B1	B2	USED ERT	USED ECT	W17 USED ERT
SP. GR.	.9996	.9992	.9992	.9990	.9978	.9976	.9990	1.0314	1.0005
VISC. 210	5.23	2.68	2.68	4.94	4.97	4.91	2.74	2.54	2.46
100	15.19	7.87	7.87	14.12	14.43	14.28	8.26	7.77	7.27
−65	1576	779	799	1426	1777	1719	1024	1289	769
mn	.03	.66	.64	.02	.02	.02	.06	.3	.05
% H2O	.14	.02	.02	.15	.14	.10	<.01	<.01	.02
AIT	890	910	NA	840	NA	NA	870	970	NA
FL. PT	330	305	315	350	330	325	320	340	315
FL PT.	375	350	350	385	365	365	355	380	350
OX. OX.	.38	.02	.09	.46	.41	.41	<.01	<.01	.11
COND.	.54	.75	.71	.54	.66	.66	.73	.8	.68
-% EPOX	0	82.1	65.2	0	0	0	57.3	80	56.4
Cl	11	1290	1334	7	5	4.4	263	237	183
HRS	0	245	264	0	0	0	498	342	418
TEMP. F.	—	262	315	—	—	—	300/284	275/262	300/284
AO'S,RAT.7	.9E702	APANA		.9 /	.45	.25-	—	—	—
AEA FC98	2XSTD	—	—	2XSTD	—	—	—	—	—
NEW AEA	NO	—	NO	NO	NO	NO	NO	NO	—
~INCR. IN INT. LEAKAGE CC'S/MIN		<600							
0 HR-RUN END 200< <500 HRS									
EROSION TYPE									
VIA;SEM									
;VISUAL									
EROSIVE,PUMP	—	YES	YES						
,BECK		—		YES					
PUMP RIG	C	—	C	C	—	—	B	A	C#1
O&c LIFE	—	—	—	—	—	—	—	—	—
SPAN @ 350 F., HRS		120		NA					

ICAP DATA:	W15/F	W15/U	W15/U	W17/F	B1	B2	W17/U	W17/U	W17/,U
Na	.94317	3.063	.606	.56	<.5	<.5	2.05	2.39	<.5
K	84.14	601.9	46.99	76.15	82.4	85.1	35	45.5	46.62
S	79.39	64.14	87.5	59.11	63.9	61.9	60.6	561.7	69.2
Cu	<.5	1213	9.811	<.5	<.5	<.5	9.32	95.76	11.34

TABLE 9-continued

Fe	<.5	43.53	293.3	<.5	<.5	<.5	8.24	60.89	50.4
Mn	<.5	.435	1.775	<.5	<.5	<.5	<.5	<.5	<.5
Zn	<.5	<.5	58.02	<.5	1.76	2.16	1.09	13.22	14.17
Al	.94	2.475	27.2	1.59	<.5	<.5	<.5	<.5	<.5
Cd	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5
	W15/F	W15/U		W17/F		W17/U		W17/U	W17/U
FOAM TEST (250/100)F (400/250)U	280/170	440/268		NA 210/93	70/25 240/130		55/18	60/20	

EXAMPLE 11

Formulations were prepared which substantially corresponded to the compositions of Example 1, except that the trialkyl phosphate and dialkyl aryl phosphate components were triisobutyl phosphate and diisobutyl phenyl phosphate, respectively, and the compositions varied with respect to the compound included as an iron corrosion inhibitor. Erosion valve leakage tests were run on these compositions in the manner described in Example 9, and epoxide depletion tests were conducted on these compositions generally in the manner described in Example 1. The results of these tests are set forth in Table 10.

The table indicates that composition M-1 used a "combination" of antioxidants. Initially, M-1 contained Ionol, Ethanox 702 and di(p-octylphenyl)amine (DODPA). After the erosion test had progressed for 25 hours, further amounts of Ethanox 702 and DODPA were added to the composition. At 153 hours, a phenolic antioxidant was added; at 267 hours, an amine antioxidant was added; and at 503 hours a mixture of Ethanox 703 and Ethanox 330 was added. Ethanox 703 is a trade designation for 2,6-di-tert-butyl-α-dimethylamino-p-cresol. The phenolic antioxidant added at 153 hours was a mixture of t-butyl phenol derivatives sold under the trade designation Iganox L-130 by Ciba-Geigy; and the amine antioxidant added at 267 hours was a reaction product of N-phenylbenzylamine and 2,4,4-trimethylpentene, sold under the trade designation L-57 by Ciba-Geigy.

compositions containing these additives exhibit satisfactory antierosion properties.

The combination of a triisobutyl phosphate/diisobutyl phenyl phosphate base stock with the 4,5-dihydroimidazole derivative of Vanlube RI-G provides a remarkable and unexpectedly favorable effect on the stability of the composition at elevated temperature. This effect is not seen with iron corrosion inhibitors other than 4,5-dihydroimidazoles of the above described type.

EXAMPLE 12

Formulations of fluid compositions were prepared in accordance with the procedure described in Example 1 using the quantities of materials and components set forth in Table 11 to demonstrate the superior characterizing properties exhibited by the fluid compositions of the present invention. The characterizing properties—determined in accordance with the procedures set forth in the Boeing Material Specification for Fire Resistant Hydraulic Fluid. BMS 2-11G (Rev. Jul. 17, 1986)— also are set forth in Table 11. In this table, "TBP" refers to tributyl phosphate; "TIBP" refers to triisobutyl phosphate; "DIBPP" refers to diisobutyl phenyl phosphate; "DBPP" refers to dibutyl phenyl phosphate; "DBPP (>99%)" refers to dibutyl phenyl phosphate of greater than 99% by weight purity; "S-154" refers to a fluid base stock component comprising about 42.8% triphenyl phosphate, about 41.7% tert-butylphenyl diphenyl phosphate, about 12.8% di(tert-butylphenyl) phenyl phosphate, 1.3% tri(tert-butylphenyl) phosphate, and 1.4% light ends and other unidentified material, all such concentrations expressed by weight; "Kronitex 100" refers to tri(isopropy-

TABLE 10

		TESTS				
		Additives		Iron Corrosion	Erosion Valve	Erosion Test Epoxide Depletion
Run	Basestock	Phenolics	Amines	Inhibitor	Leakage	@ 300° F.
W-1	TIBP/DIBPP	Continuation	Combination	None	<100 cc	>95%[a]
W-2	TIBP/DIBPP	E703/E330	DODPA	None at the start. At 22 hrs. Petrolite 31001 added.	>200 cc	65%[a]
W-3	TIBP/DIBPP	Ionol/E702	DODPA	Vanlube RI-G	100 cc	22%[a]
W-4	TIBP/DIBPP	Ionol/E702	DODPA	Vanlube RI-G	—	78.9%[b]
W-5	TIBP/DIBPP	Ionol/E702/E330	DODPA	Vanlube RI-G	—	58%[a]

[a]Boeing BMS-3-11G Erosion Resistance Test
[b]Boeing, BMS-3-11G, Erosion Control Test

These data and those of Example 9 demonstrate that the iron corrosion resistance agents Petrolite 31001 and vanlube RI-G are both satisfactory with respect to effect on erosion. Neither appears to significantly accelerate erosion, and the

lphenyl) phosphate commercially available from FMC Corporation; "6703", "6770", "6477", and "6961-PMN" refer to poly(alkyl methacrylate) viscosity index improvers commercially available from Rohm and Haas Company; "HF411" and "HF460" refer to poly(butyl/hexyl methacrylate) viscosity index improvers; "C_6–C_{10} polyacrylate" refers to a viscosity index improver, commercially available from Union Carbide Corporation; "FC-98" refers to an antierosion agent comprising a potassium salt of perfluorooctylsulfonic acid, also known as perfluorooctanesulfonic acid; "NH4PF6/Ca(SO3DF3)2" refers to an antierosion agent comprising a mixture of ammonium hexafluorophosphate (NH_4PF_6) and calcium di(perfluoromethanesulfonate) [$Ca(SO_3CF_3)_2$]; "MCS 1562" refers to 2-ethylhexyl 3,4-epoxycyclohexanecarboxylate, an acid scavenger, described in U.S. Pat. No. 3,723,320; "ERL 4234" refers to 2-(3,4-epoxycyclohexyl)-5,5-spiro(3,4-epoxy)cyclohexane-m-dioxane, an acid scavenger, commercially available from Union Carbide Corporation; "DODPA" refers to di(p-octylphenyl)amine, an antioxidant; "Ionol" refers to 2,6-di-tert-butyl-p-cresol, an antioxidant, commercially from Shell Chemical Company; "E-702" refers to bis(3,5-di-tert-butyl-4-hydroxyphenyl)methane, an antioxidant, commercially available under the trade designation Ethanox® 702 from Ethyl Corporation; "E-330" refers to 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenyl)benzene, an antioxidant, commercially available under the trade designation Ethanox® 330 from Ethyl Corporation; "KOPHEN" refers to potassium phenate; "P-57068" refers to a benzotriazole derivative, a copper corrosion inhibitor, commercially available under the trade designation Petrolite 57068 from Petrolite Corporation; "FH-132" refers to 1,2-di(phenylthio)ethane, a copper corrosion inhibitor; "P-31001" refers to an iron corrosion inhibitor, commercially available under the trade designation Petrolite 31001 from Petrolite Corporation; "Vanl RI-G" refers to the condensation product of 4,5-dihydro-1H-imidazole and C_{16}–C_{18} fatty acid commercially available under the trade designation Vanlube RI-G from Vanderbilt Company; "Sarkosyl-O" refers to N-methyl-N-(1-oxo-9-octadecenyl)glycine commercially available under the trade designation Sarkosyl®-O from Ciba-Geigy Corporation; and "Unamine C" refers to 1-hydroxyethyl-2-coca-imidazoline, an iron corrosion inhibitor.

TABLE 11[1]

	Skydrol ® LD-4[2]	Hyjet ® IVA[3]	1[4]	2[4]	3[5]	4[6]	5[7]	6[8]	7[9]	8[10]	9[11]	10[11]	11[11]	12[12]	13[13]
Phosphate Ester Base Stock															
TBP	50–60	72.60	67.00	67.00											
TIBP					69.00	62.00	87.55	82.90	65.51	69.10	84.35	84.35	84.40	84.61	86.60
DIBPP					22.00	20.00	10.00	5.00							
DBPP	30–35		22.30	22.30											
DBPP (>99%)									20.54	18.00					
S-154											3.00	3.00	3.00	3.00	
Kronitex 100		11.80													
Viscosity Index Improver															
6703								4.65	5.50	4.70	4.50	4.70	4.65		5.25
6770					6.30	4.50	4.50								
6477			7.50	7.50											
6961-PMN														4.65	
HF411	5–10														
HF460															
C_6 –C_{10} Polyacrylate		6.00													
Anti-Erosion Agent															
FC-98, ppm	0.005–1.00		500	500	500	500	250	250	250	250	250	250	250	250	250
NH_4PF_6/Ca $(SO_3CF_3)_2$		0.078													
Acid Scavenger (Epoxide)															
MCS 1562	4–8		6.30	6.30	6.30	6.30	5.80	5.80	6.30	6.00	6.00	5.80	5.80	5.80	6.00
ERL 4234		1.9–2.3													
Antioxidant															
DODPA		1.00	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Ionol	1.00	0.50	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
E-702			0.90	0.90	0.90	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
E-330						0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
KOPHEN, ppm			350	350	350	350									
Copper Corrosion Inhibitor															
P-57068			0.05	0.05	0.05	0.05									
FH-132	0.13–1.00						0.50		0.50	0.50	0.50	0.50	0.50	0.50	0.50
Iron Corrosion Inhibitor															
P-31001			0.05												
Vanl.RI-G, ppm				250	250	250	250	250	250	250	250	250	250	250	250
Sarkosyl-O															
Unamine C		0.15													
Water		0.23	0.14		0.15	0.15			0.09				0.15		
Char. Properties															
Acidity		0.09	0.02		0.1	0.1			0.04				0.03		
Viscosity, cst															

TABLE 11[1]-continued

	Skydrol ® LD-4[2]	Hyjet ® IVA[3]	1[4]	2[4]	3[5]	4[6]	5[7]	6[8]	7[9]	8[10]	9[11]	10[11]	11[11]	12[12]	13[13]
@-65° F. (-53.8° C.)	1185	1353	1777		3957	2720	1945	1778	2438	1822	1899	2045	1886	4226	1831
100° F. (37.8° C.)	11.42	10.81	14.40		13.51	9.29	8.76	8.89	11.15	9.46	8.86	9.09	9.05	12.11	9.47
210° F. (98.9° C.)	3.93	3.62	5.00		4.28	3.09	2.95	3.03	3.69	3.17	2.98	3.07	3.08	3.75	3.21
Thermal Stability, hr. @325° F. (162.8° C.)	~300	—	677	420	1264	1251			929	>900					1800
Bulk Modulus, psi	221,000	246,000	212,000	—	201,000	201,000	211,000		215,000	216,000	210,000	209,000			205,000
Autoignition Temp., °F./°C.	880/471.1	800/426.7	870/465.6		950/510	950/510			900/482.2	900/482.2	890/476.7		880/471.1		880/471.1

[1]Except as otherwise indicated, amounts of components are expressed as % by weight.
[2]Skydrol ® LD-4 aircraft hydraulic fluid; commercially available from Monsanto Company.
[3]Hyjet ® IVA aircraft hydraulic fluid; commercially available from Chevron International Oil Company.
[4]The phosphate ester base stock comprises 75.03% by weight TBP and 24.97% BY WEIGHT DBPP.
[5]The phosphate ester base stock comprises 75.82% TIBP and 24.18% by weight DIBPP.
[6]The phosphate ester base stock comprises 73.81% TIBP and 24.39% by weight DIBPP.
[7]The phosphate ester base stock comprises 89.75% TIBP and 10.25% by weight DIBPP.
[8]The phosphate ester base stock comprises 94.31% TIBP and 5.69% by weight DIBPP.
[9]The phosphate ester base stock comprises 76.13% TIBP and 23.87% by weight DBPP (>99%).
[10]The phosphate ester base stock comprises 79.33% TIBP and 20.67% by weight DBPP (>99%).
[11]The phosphate ester base stock comprises 96.57% TIBP, and 3.43% by weight triaryl phosphate [tri-phenyl phosphate (TPP) - 42.8%, tert-butylphenyl diphenyl phosphate (TBPDP) - 41.7%, di(tert-butylphenyl) phenyl phosphate (DTBPPP) - 12.8%, and tri(tert-butylphenyl) phosphate - 1.3% (TTBPP), and 1.4% light ends and other unindentified materials].
[12]The phosphate ester base stock comprises 96.58% TIBP and 3.42% by weight triaryl phosphate (42.8% TPP, 41.7% TBPDP, 12.8% DTBPPP, and 1.3% TTBPP).
[13]The phosphate ester base stock comprises 100.00% by weight of TIBP.